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**CHEMICAL FRACTIONATIONS  
IN METEORITES**

*by Edward Anders*

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UNIVERSITY OF CHICAGO  
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## CHEMICAL FRACTIONATIONS IN METEORITES\*

Edward Anders

For many years chondrites have been accepted as average samples of non-volatile planetary matter, and have served as the basis of the cosmic abundance curve. There are two reasons for this acceptance: the abundances in chondrites resemble those in the sun, and they seem to be a smooth function of mass number. But the latter rule had its exceptions from the very beginning. In 1947, when Suess (1) attempted to construct a semi-empirical cosmic abundance curve on the basis of Goldschmidt's (2) meteoritic data, he noted that certain elements (Se, Te, Ga, In, Tl, Zn, Cd, Hg, and Re) were underabundant relative to their neighbours. Since most of these elements were congeners in the Periodic Table, he suggested that chemical factors were responsible for their depletion. Subsequent work showed some of these measurements (Ga, Re) to be erroneous, and for a while it was believed that all such discrepancies would eventually disappear.

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\*This paper is an abridged version of a talk given at the 11th Meteorite Conference of the Academy of Sciences of the USSR, Moscow, May 26-30, 1964.

But this was not so. Precision measurements by neutron activation analysis have tended to confirm or even enlarge these discrepancies, and have led to the discovery of still others. Moreover, Reed et al (3) made an important observation: elements which are depleted by factors of 10-1000 in ordinary chondrites (e.g. Hg, Tl, Pb, and Bi), often occur in nearly their predicted, "cosmic" abundances in carbonaceous and enstatite chondrites. But even within these two classes the abundances scattered considerably.

It seems that sufficient data have accumulated by now for some trends to be recognized. Let us begin by considering the carbonaceous chondrites (Figure 1). We have included in this graph only those elements whose abundances are known or suspected to be variable. Insofar as possible, the elements have been grouped according to their chemical properties. To reduce the data to a common basis, they have been converted to "depletion factors", defined as the ratio of cosmic to observed abundance. This notation perhaps looks a little awkward at first, but it has the advantage that a large depletion corresponds to a large depletion factor. The cosmic abundances were taken from Cameron's table (4), which relies rather extensively on carbonaceous chondrite data. Actually this choice introduces very little bias, since we shall be concerned mainly with the relative position of the points, which is independent of the normalization standard on a logarithmic plot.

Easily the most striking feature of this graph is the consistent difference among the three subclasses of carbonaceous chondrites (5, 6). Type III invariably has the highest depletion factor, followed by Types II and I.\* Moreover, the relative depletion factors are remarkably constant, as implied by the nearly constant separation of the curves. Type II usually lies a factor of 2 above Type I; and Type III, a factor of 4. This relationship seems to be nearly independent of the absolute size of the depletion factor; it holds equally well for depletion factors of  $10^4 - 10^5$  (Kr, Xe, H) and 1 - 100 (the remaining elements).

Most surprising is the fact that this trend is shared by such a diverse group of elements. All major geochemical classes are represented: atmophile elements (Kr, Xe, F, Cl), lithophile (Na, K, Rb, Cs), chalcophile (S, Zn, Cd) and siderophile (Ge). Why should elements as different in their geochemistry as Xe, Rb, F, S, Cd, Pb, and Ge all be depleted to the same relative degree?\*\*

Obviously, conventional geochemical classifications are of little use in explaining this fractionation. The only property

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\*The points at Bi are the only exception to this rule. But they are based on single measurements only (3), and the apparent inversion may well be due to experimental error.

\*\*Zähringer (7) was the first to note the curious fact that the heavy noble gases follow the trend of other heavy elements.

all these elements share to a greater or lesser degree is their volatility. Does this mean that these elements were depleted in Types II and III by reheating, or by accretion at higher temperatures? Most certainly not. In his discussion of trace metal volatilization from ordinary chondrites and the earth, Urey (8, 9, 10) pointed out that an element or compound remains gaseous if its vapor pressure exceeds the pressure of the nebular gas; otherwise it condenses. Accordingly, an all-or-nothing type of fractionation results. Even slight differences in volatility must lead to large differences in the degree of retention. Had meteoritic matter separated at high temperatures from its cosmic complement of gases, the elements Zn, Se, Cd, and Te should have been preferentially lost, by factors comparable to those of the noble gases ( $\approx 10^7$ ). The data then available indicated little or no depletion of these elements, and Urey therefore concluded that meteoritic and terrestrial matter separated from the nebula and accreted at low temperatures, where all volatile trace elements would be retained.

Urey's argument about the high selectivity of volatilization processes applies with even greater force to the present situation. Why should xenon (B.P. =  $-107^\circ\text{C}$ ), hydrocarbons (B.P. =  $200-500^\circ\text{C}$ ), cadmium (B.P. Cd =  $767^\circ\text{C}$ , CdS  $\approx 1320^\circ\text{C}$ ), and lead (B.P. Pb =  $1620^\circ\text{C}$ , PbS =  $1280^\circ\text{C}$ ) all show the same relative depletions among Types I, II, and III?

It seems that no model involving a common, unitary history of chondritic matter can account for this abundance pattern.

One is driven to the assumption that chondritic matter is a mixture of at least two kinds of material of widely different chemical histories. The simplest model that seems capable of accounting for the evidence assumes that carbonaceous chondrites are mixtures of two types of material: an undepleted fraction (= A) containing all the "deficient" elements, and a depleted fraction (= B) containing none. Fraction A may have separated from its cosmic complement of gas at low temperatures and therefore retained its volatiles, while fraction B became separated\* from its gases at high temperatures and therefore lost its volatiles. If Types II and III contained only  $1/2$  and  $1/4$  as much of fraction A as Type I, then the uniform depletion by factors of  $\approx 2$  and  $\approx 4$  would be explained.

Is there any evidence that the carbonaceous chondrites consist of two dissimilar fractions? Apparently so. DuFresne and Anders (11) showed that the proportion of "high-temperature minerals" (olivine, pyroxene, and metal) decreased drastically from Types III to I (Fig. 2). The observed amounts of these minerals agree remarkably well with the postulated amounts of fraction B, namely  $\approx 3/4$ ,  $1/2$ , and 0.\*\*

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\*This separation need only be chemical, not necessarily also physical. The essential point is that the solids ceased to react chemically with the gases while the temperatures still were high.

\*\*DuFresne and Anders suggested that the decrease was due to progressive destruction of these minerals by water solutions. I now believe that this process was only of subordinate importance, the major part of the low-temperature minerals being of primary origin.

This compositional correlation is paralleled by a structural one. Type III carbonaceous chondrites consist largely of chondrules, with only a modest amount of matrix. Type I consist of matrix only, and Type II, of roughly equal amounts of chondrules and matrix. Thus the relative amounts of matrix and chondrules agree rather well with the postulated amounts of fractions A and B.

Tentatively, one can therefore identify fractions A and B with the matrix and chondrules, consisting of low- and high-temperature minerals respectively. It must be emphasized that this identification is tentative. There is as yet no evidence that these two fractions differ in their trace element content, as required by our model.

It will be instructive to examine the data for other types of chondrites, to see whether they are consistent with our model. Figure 3 gives the depletion factors for ordinary and enstatite chondrites. For comparison, the data on carbonaceous chondrites are also shown.

Ordinary Chondrites. Of the thirteen deficient elements between F and Bi, nine (F, S, Cl, Zn, Ge, Cd, Te, I, and Hg) show depletion factors of 3 - 12. The highest three values are associated with the more volatile of these elements: Cd, Hg, and I (e.g., B.P.  $\text{CaI}_2 = 718^\circ\text{C}$ ), but the remaining ones again show the surprising sameness we encountered in the Type II and III carbonaceous chondrites. Nevertheless, certain important differences are evident.



- (1) The alkali elements are not depleted.
- (2) There appears to be some excess depletion of Cd, Hg, and I, particularly if the abundances are compared with those in Type I carbonaceous chondrites, rather than with the cosmic abundance curve. Xenon, though not plotted, also seems to fit this trend.
- (3) In, Tl, Pb, and Bi are depleted by still larger factors.

In view of these exceptions, one might be tempted to discard the model altogether. But then one is faced with the problem of explaining the constancy of the depletion factors of F, S, Cl, Zn, etc., and thus one is led right back to a two-component model. Perhaps the best approach is to retain the model, and augment it by such ad hoc assumptions as are needed to account for the exceptions. If the model has any reality to it, these "exceptions" may actually provide clues to the formation (or accretion) conditions of the several chondrite classes. After all, we have no assurance that all classes of meteorites formed under exactly identical conditions.

The non-depletion of alkali metals requires that fraction B of ordinary chondrites condensed at sufficiently low temperatures and high pressures to prevent volatilization of alkalis. The preferential depletion of Cd, Hg, I ( and Xe) means either that these elements were partially lost during metamorphism, or that fraction A in ordinary chondrites is of composite nature. (One part must have lost its gases at low enough temperatures to retain these elements, while another, major part must have condensed

at higher temperatures where they were lost.) The depletion of In, Tl, Pb, and Bi is a mystery. Except for organo-metallic compounds, no outstandingly volatile compounds of these elements are known. Their depletion points to some unique circumstance in the formation of ordinary chondrites, but it is not obvious what this circumstance was.

Enstatite Chondrites. For the purposes of this paper, these meteorites have been divided into two subclasses. Type I includes Indarch, Abee, and St. Sauveur. Type II includes the remaining members of this class. (A similar classification was proposed by Yavnel' several years ago). Type I shows only a slight depletion relative to carbonaceous chondrites of Type I, except for Hg. Type II is more strongly depleted, however. For S, Cl, Ge, Te, and I the depletion factors are 1.5 - 4 times higher than those of the Type I enstatite chondrites. In terms of our model, this merely implies that they contain a smaller amount of fraction A. The selective depletion of Zn and Cd probably calls for the same explanation that was invoked in the case of the ordinary chondrites.

Iron Meteorites. A virtue of this model is that it can also account for the remarkable Ga and Ge groups of Goldberg et al (12) and Lovering et al (13). Figures 1 and 3 show that Ge is a depleted element which, according to our model, is brought in by fraction A. The data for Ga are incomplete, but since the Ga abundance in ordinary chondrites is a factor of 3.3 lower than its interpolated cosmic abundance [39; ref. (4)], Ga

is probably also a depleted element which is brought in by fraction A. Now, both Ga and Ge are known to be strongly siderophile in meteorites, and it therefore seems likely that iron meteorites have retained the major part of the Ga and Ge that was originally present in their parent substance. But, in terms of our model, the Ga and Ge content of their parent substance was determined entirely by the proportion of fraction A. Hence the present Ga and Ge content of an iron meteorite should be a reliable and characteristic measure of the proportion of fraction A in their parent substance.

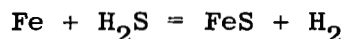
The gallium contents of all meteorites analyzed by Goldberg et al and Lovering et al are shown in Figure 4. In comparing meteorites of different Ni content, it is well to remember that Ga and Ni are both siderophile. Meteorites derived from material of the same Ga content will therefore have a constant Ga/Ni ratio, regardless of what fraction of iron has been removed as troilite or silicate. One such curve of constant Ga/Ni ratio is shown at the top of Figure 4. This particular curve corresponds to the cosmic Ga/Ni ratio according to Cameron (4). Other curves of constant Ga/Ni ratio must run parallel to it.

Evidently Groups I and II fall quite close to the "cosmic" Ga/Ni line. If we trust the cosmic Ga/Ni ratio, we can conclude that these meteorites are derived from material consisting largely, i.e. to  $\approx 70 - 100\%$ , of fraction A. Groups III and IV would seem to correspond to about 20% and 2% of fraction A. The

first two groups thus match the carbonaceous and enstatite chondrites of Types I, while Group III matches the ordinary chondrites. While this correlation is not specific enough to prove a genetic link, it is in partial agreement with the relationships deduced earlier by Yavnel' (6). In terms of our model, each family of meteorites characterized by a particular depletion factor for Ga, Ge, and other elements is derived from a separate batch of primitive matter, perhaps a separate parent body.

It is of some interest to see which of the existing theories on the origin of meteorites explicitly provide for the principal feature of this model: a dual origin of meteoritic matter. Apparently only Wood's theory contains this feature. Wood (14, 15, 16, 17) proposes that all meteoritic matter passed through a high-temperature, high-pressure stage very early in its history, while it was still dispersed in the protosun or solar nebula. On cooling, one part of the material passed through the liquid field of the phase diagram and condensed to millimeter-sized droplets of silicate (= chondrules) and metal. Owing to their small specific surface, these particles would be chemically isolated from the cooling gas, even if the physical separation from the gas did not happen until later. Another part of the material missed the liquid field and condensed directly from vapor to solid, presumably in the form of a fine smoke, which later became the matrix of chondrites. These particles, being less than a micron in size (16), would have a much larger specific surface than the chondrules and metal particles. They would

therefore remain in equilibrium with the gas phase down to rather low temperatures where volatiles could be adsorbed, and where metallic iron would revert to FeS and  $\text{Fe}_3\text{O}_4$ :



In a gas phase with cosmic ratios of  $\text{H}_2/\text{H}_2\text{S}$  and  $\text{H}_2/\text{H}_2\text{O}$ , the first reaction goes from left to right below  $600^\circ\text{K}$ , and the second, below  $390^\circ\text{K}$  (8).

Wood's mechanism thus produces two fractions that closely correspond to our fractions A and B. Two slight differences remain. Wood requires that his chondrules-plus-metal fraction passed through the liquid field, whereas our definition of fraction B merely requires that it became separated from its gases at high temperatures. Our definition thus includes angular and fine-grained material that did not pass through the liquid field: The proportion of fraction B in a given chondrite may therefore be larger than the proportion of chondrules and metal grains. Another difference exists between fraction A and the matrix. Wood's definition states that the matrix, like our fraction A, became separated from its gases at low temperatures, but imposes the additional requirement that it was previously heated to high temperatures and vaporized. Actually the retention of volatiles in cosmic proportions would be easier to understand if fraction A were the primordial dust itself, rather than a vaporized and recondensed derivative of it. But this is not an unbridgeable difference. In the latest version of Wood's theory,

the high temperatures and pressures are produced in the nebula on a purely local scale, by shock waves associated with giant flares of the early sun. Now, if this condensation process happens only locally, one may expect wide compositional variations in the nebula. Some regions may consist mainly of unaltered primordial dust; others, of reheated and recondensed material; still others, of mixtures of both, or of slightly reheated primordial dust. Certainly the variations in the condensation conditions of fractions A and B in various meteorite classes are entirely consistent with the range of variations expected in Wood's model. If accretion was rapid, such differences would persist in the individual meteorite parent bodies.

If this model is correct, then the material of the achondrites, the earth, and the other planets may have been fractionated by the same mechanism. Gast (18) and more recently, Wasserburg et al (19) have proposed that the earth has a lower alkali content than do the ordinary chondrites. Inasmuch as fraction B of the carbonaceous chondrites shows evidence of alkali metal depletion by volatilization, there is no reason why the earth should not have lost some of its alkalis in the same manner, if it, too, accreted from two types of "primordial" matter. In fact, if the above model is valid, one should be able to reconstruct the formation conditions of the earth from the abundances of the 30-odd depletable elements in Figure 1. Similarly, the low alkali content of the calcium-rich achon-

drites, which has been the subject of much speculation, may also be an early feature, reflecting accretion from a strongly-heated, alkali-poor fraction B. It would be an interesting and perhaps not entirely pointless exercise to reconstruct genetic relationships among meteorites on the basis of trace element content.

#### SUMMARY

1. It is not possible to find a single set of chemical and physical conditions that is consistent with the abundance pattern in chondrites. Instead, it must be assumed that meteoritic matter is derived from at least two materials of contrasting chemical history. This conclusion is firm.

2. The simplest model that accounts for the present data assumes that the meteorites (and planets) are a blend of two types of material: an undepleted fraction A rich in volatiles, and a depleted fraction B from which the volatiles were lost. The first apparently became separated from its cosmic complement of gas at a low temperature, and the second, at a high temperature.

3. Tentatively, one can identify fractions A and B with low-temperature and high-temperature minerals in primitive, unmetamorphosed chondrites. They also correspond roughly to the matrix and chondrules-plus-metal fractions.

4. Wood's theory (17) with a few minor modifications, provides a rather satisfactory framework for the origin of fractions A and B. Fraction A is unreheated or slightly reheated primor-

dial dust, while fraction B is primordial dust that was vaporized and recondensed during passage of a shock wave through the solar nebula, and became chemically isolated from its gases at high temperatures.

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### FIGURE CAPTIONS

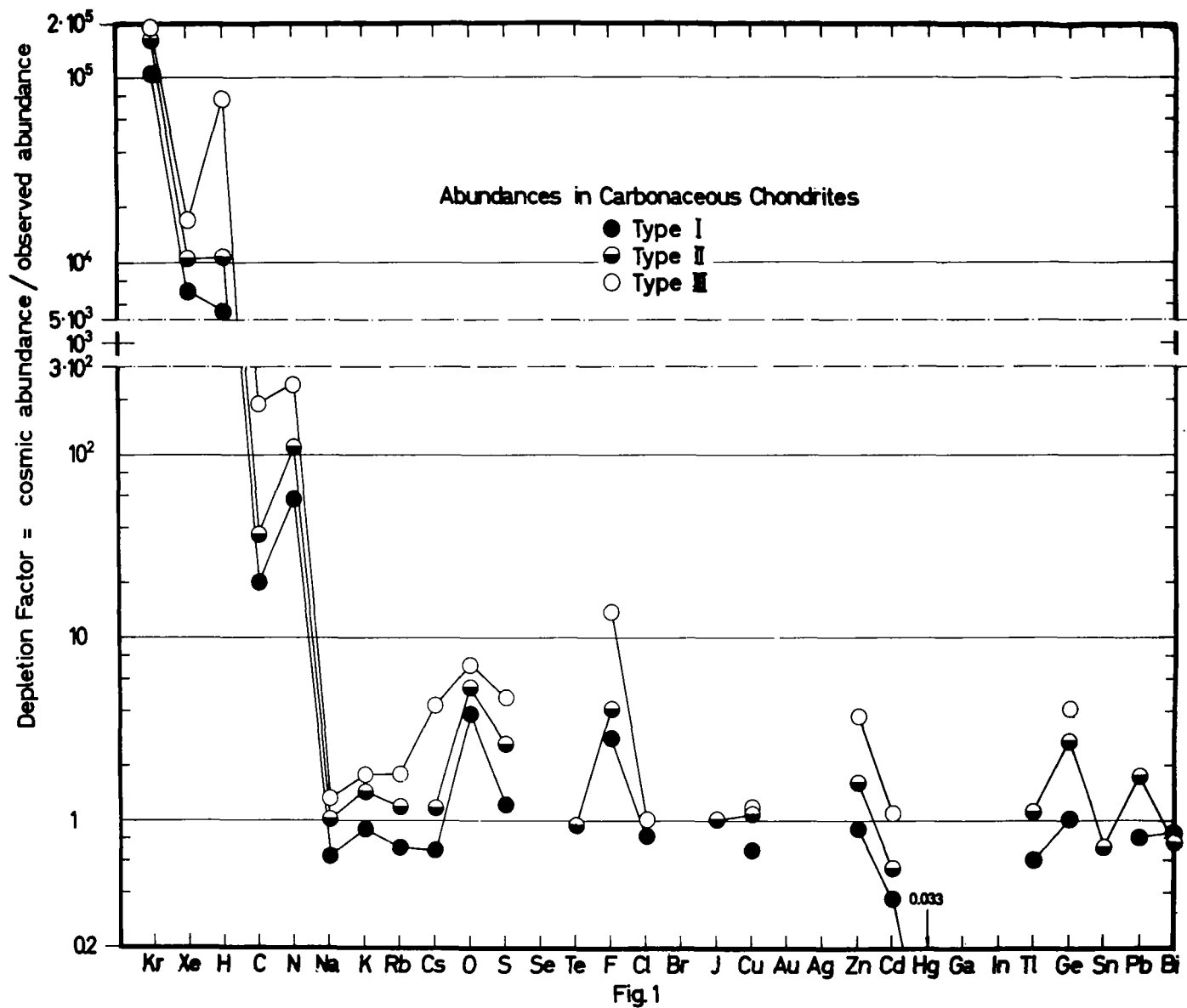
Figure 1. Abundances of various depleted elements in carbonaceous chondrites. Relative to Type I carbonaceous chondrites, Types II and III usually show depletions by nearly constant factors of  $\approx 2$  and  $\approx 4$  respectively. This correlation holds for elements as dissimilar as Xe, Na, S, F, Cd, and Ge. The data were taken from the following sources: Kr, Xe, Zähringer (7); H, C, N, Na, K, O, S, Cu, Mason (20); Cs, Smales et al (21); Cl, Zn, Ge, Greenland (22), Nishimura and Sandell (23), Nishimura and Nasu (24), Shima (25); Te, I, Goles and Anders (26); F, Reed (27), Fisher (28); Cd, Schmitt et al (29); Hg, Tl, Bi, Pb, Reed et al (3); Sn, Shima (25).

Figure 2. Approximate mineralogical composition of carbonaceous chondrites. The proportion of low-temperature minerals decreases from Type I to Type III. [Based on the data of DuFresne and Anders (11)].

Figure 3. Abundances of depleted elements in various types of chondrites. The correlation for ordinary and enstatite chondrites is less perfect than that for carbonaceous chondrites, but again there is a marked tendency for the curves to run parallel over extended stretches. The data were taken from the same sources as in Figure 1, and the following additional ones: N, König et al, (30); In, Schindewolf and Wahlgren (31); Hg, Tl, Pb, Bi, Ehmann and Huizenga (32); major elements, Urey and Craig (33).

FIGURE CAPTIONS CONT'D.

Figure 4. Gallium groups of irons and stony irons. Adapted from Goldberg et al (12) and Lovering et al (13). The curve in the upper left-hand corner corresponds to the cosmic Ga/Ni ratio (4). All meteorites derived from material of the same Ga content should lie on a line parallel to the "cosmic" curve. Most meteorites in Groups I and II lie close to the "cosmic" curve, but the other two groups are strongly depleted.



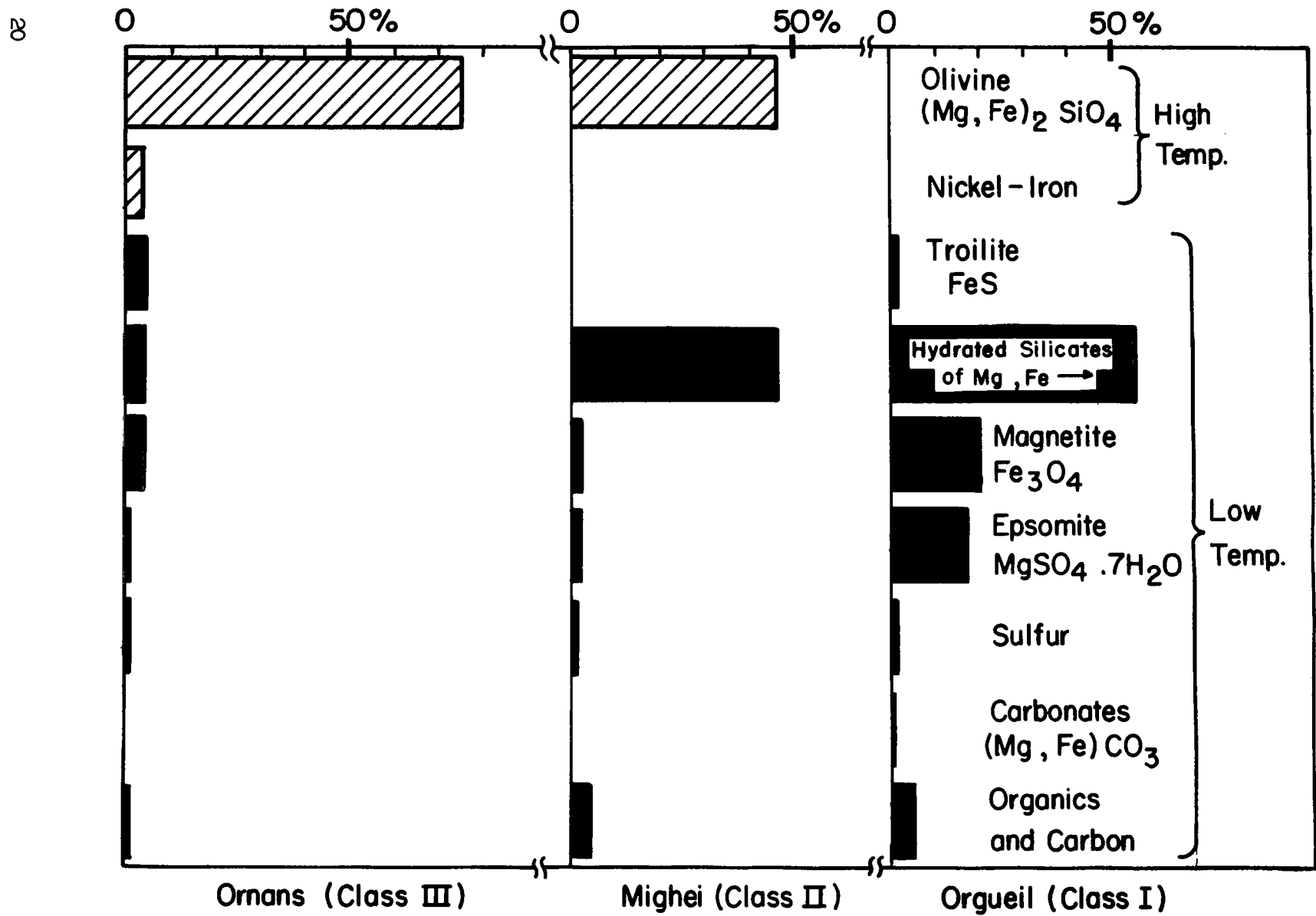


Fig.2

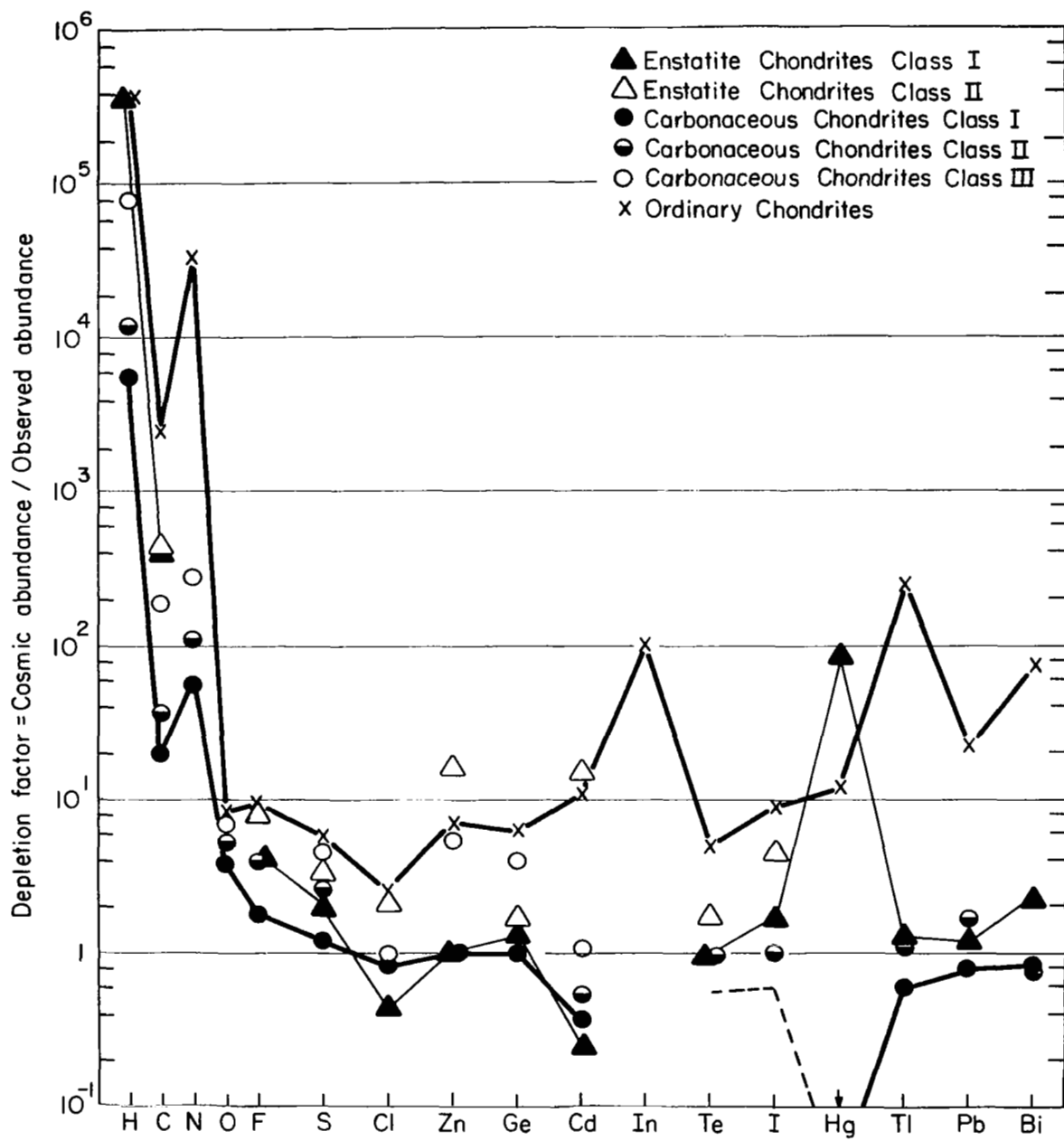


Fig.3

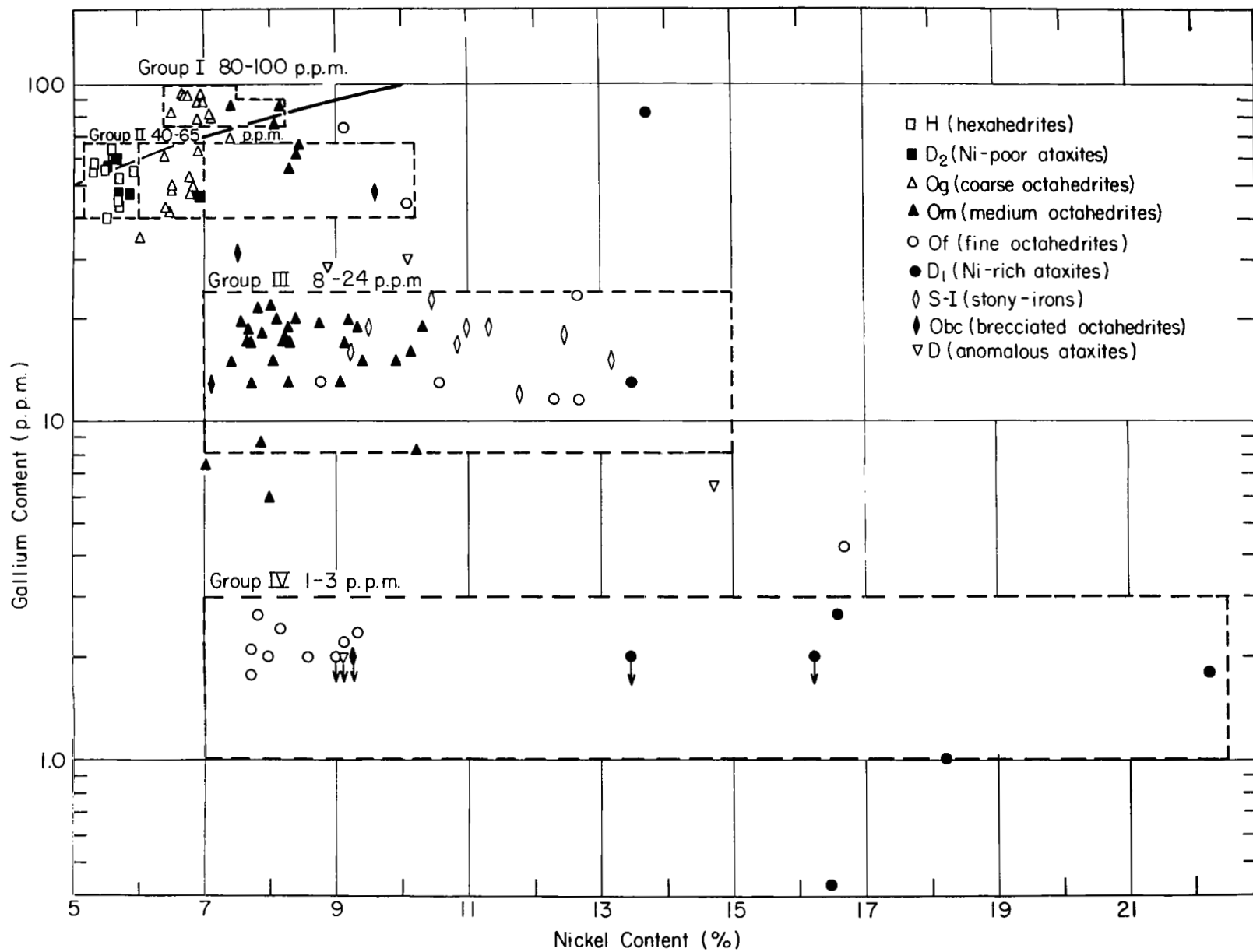


Fig.4